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(54) Disinfectant compositions

(57) A solid composition, suitable for use in in the preparation of a rapidly effective cleaning, sanitizing or sterilising solution, comprises an organic peracid precursor, a per-salt and a biocidal quaternary ammonium compound.

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FIGURE 1

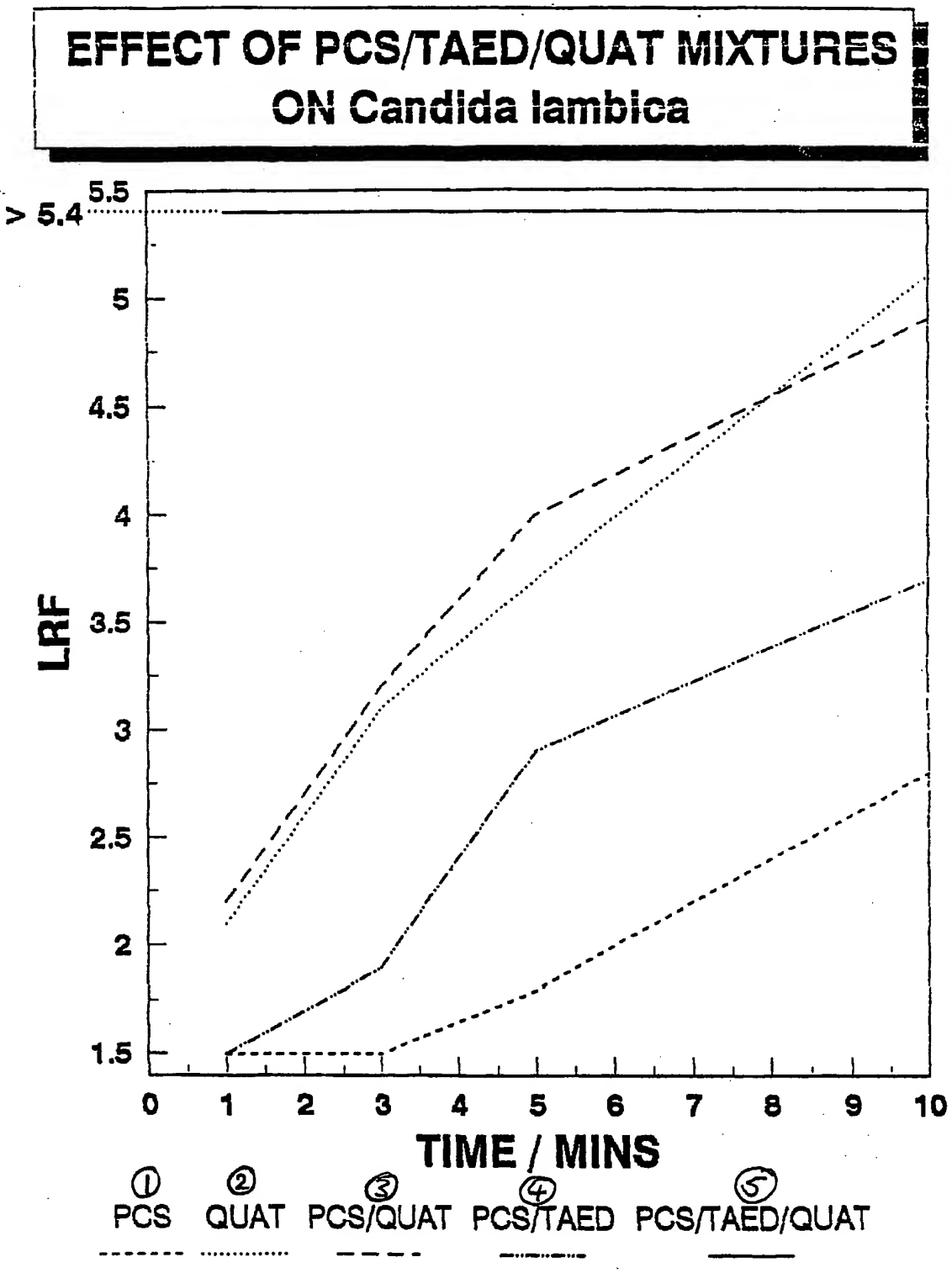
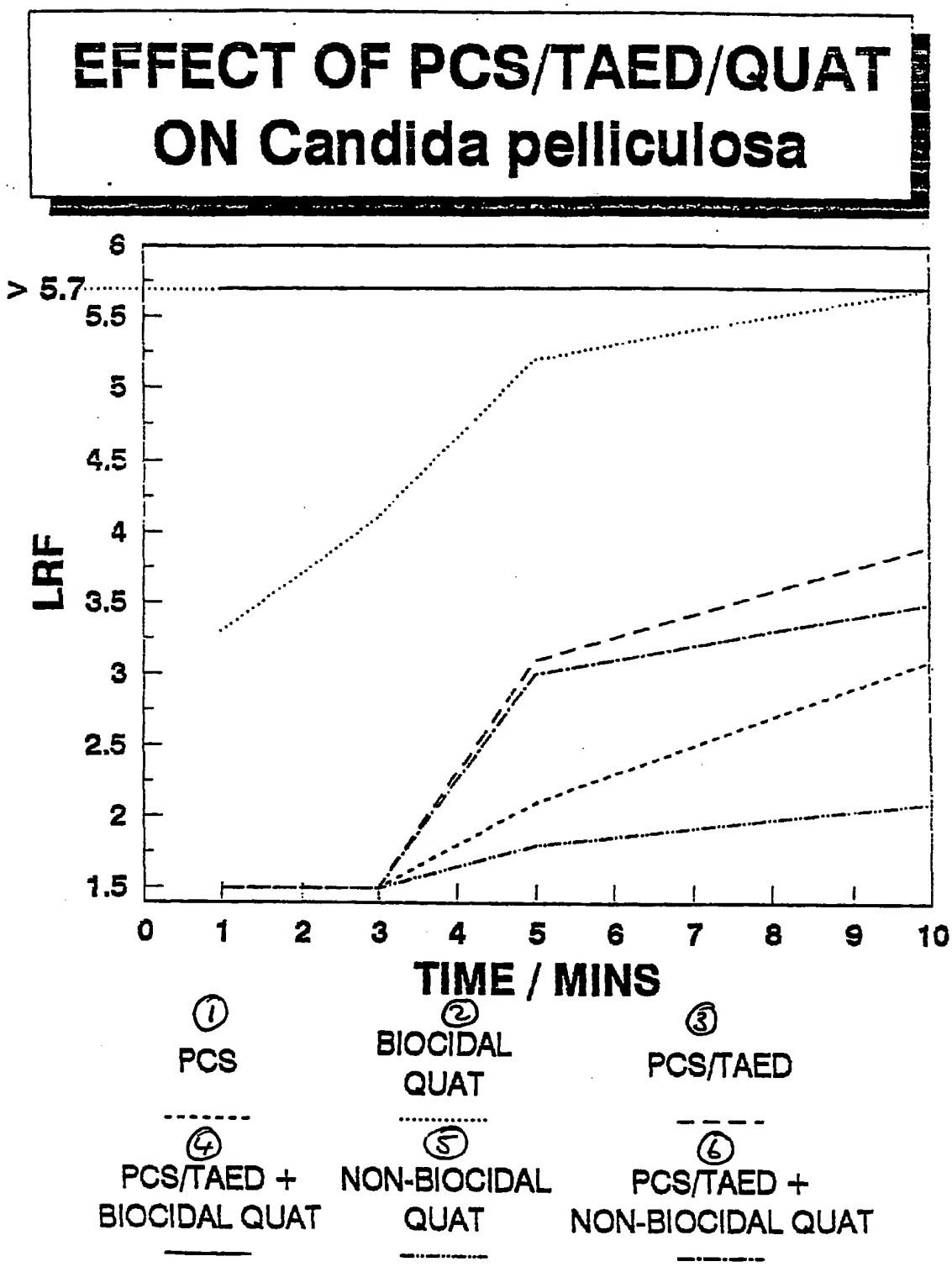

EFFECT OF PCS/TAED/QUAT MIXTURES
ON Candida lambica
> 5.4
5.5
5
4.5
4
3.5
3
2.5
2
1.5
LRF
0
1
2
3
4
5
6
7
8
9
10
TIME / MINS
① PCS
② QUAT
③ PCS/QUAT
④ PCS/TAED
⑤ PCS/TAED/QUAT

FIGURE 2


EFFECT OF PCS/TAED/QUAT
ON Candida pelliculosa
LRF
> 5.7
6
5.5
5
4.5
4
3.5
3
2.5
2
1.5
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1
2
3
4
5
6
7
8
9
10
TIME / MINS
① PCS
② BIOCIDAL QUAT
③ PCS/TAED
④ PCS/TAED + BIOCIDAL QUAT
⑤ NON-BIOCIDAL QUAT
⑥ PCS/TAED + NON-BIOCIDAL QUAT

Compositions

This invention is concerned with compositions which are useful in the preparation of cleaning, disinfecting, sanitising and sterilising compositions. More particularly, the present invention is concerned with solid compositions which when dissolved in an appropriate solvent form compositions comprising organic peroxygenated acids and biocidal quaternary ammonium compounds (QAC's) useful in or as cleaning, sanitising and sterilising compositions.

It is known that peracetic acid (PAA) and certain QAC's have biocidal activity and this fact has been exploited in the past by incorporating the compounds individually into, for example, cleaning, sanitizing and sterilising compositions used in hospitals and dairies.

PAA based compositions are most effective at acidic pH's, whereas the QAC based compositions are most effective at alkaline pH's.

WO 88/00795 discloses an antiseptic composition comprising PAA, alkyldimethylbenzyl ammonium chloride and an essential oil.

In US-A-4847089 and US-A-4850729 there are disclosed dry, water-activated compositions comprising per-salts and phase-transfer agents which are useful for preparing disinfectants and cleansing and decontaminating agents. These compositions, however, tend to be relatively slow acting, requiring more than 5 minutes from addition of the solid composition to water for the resulting disinfectant or cleansing and decontaminating agent to be effective against microbes.

It is an object of the present invention to provide a dry composition which may be used for preparing relatively fast acting cleaning, disinfecting, sanitising and sterilising compositions .

In accordance with the present invention there is provided a dry composition suitable for use in the preparation of aqueous cleaning, sanitizing or sterilising composition, characterised in that the composition comprises an organic peroxyacid precursor, a persalt, and a biocidal quaternary ammonium compound. Any biocidal QAC is suitable for use in the compositions of the present though, for storage stable solutions, preferably, the QAC has a non-halogen or non-halogenated anion. More preferably, the QAC is a non-halogenated QAC, where both the anion and cation of the QAC comprise groups other than halogen or halogenated groups. Surprisingly, the compositions of the present invention are relatively fast acting, in that when made into a solution, e.g. an aqueous solution, the solution requires substantially less than 5 minutes, e.g. less than 1 minute, to be effective against microbes at ambient temperature

(20°C). Furthermore, within the first 5 minutes from when a composition of the present invention is added to an appropriate solvent, the resulting composition demonstrates synergistic improvements in effectiveness against microbials over the per-salt and QAC alone or together and over the per-salt and precursor together.

The weight ratio of precursor:per-salt in the composition is preferably from about 4:1 to about 1:20, more preferably from about 1:1 to about 1:10, and most preferably from about 1:2 to about 1:5.

The weight ratio of precursor and per-salt:QAC in the composition is preferably from about 1:1 to about 1:30, more preferably from about 1: to 1:20, and most preferably from about 1:2 to about 1:10.

The per-salts and precursors may be completely soluble or only sparingly soluble in the appropriate solvent, but each must dissolve to such an extent to enable formation of peroxyacid in a sufficient quantity, as will be readily appreciated by the skilled person.

The peroxyacid precursors used in the present invention are compounds which, in the appropriate solvent and in the presence of the per-salt, generate organic peroxyacids The peroxyacids which may be generated from the precursors useful in the composition of the present invention are preferably organic peroxycarboxylic acids, more preferably C_2-C_{10} aliphatic peroxyacids, e.g. peracetic acid (PAA) and pernonanoic acid (PNA). The peracid may be unsubstituted or substituted. The preferred precursors are tetra acetyl ethylene diamine (TAED), sodium nonanoyl oxy benzene sulphonate (SNOBS) and penta acetyl glucose (PAG). The most preferred precursor is TAED and, consequently, the most preferred peroxyacid is PAA.

The per-salts used in the present invention are salts having hydrogen peroxide of crystallisation or salts which when dissolved in an appropriate solvent release peroxygen or peroxide ions. Such salts are well known to the skilled person. Examples of suitable per-salts are selected from the group consisting of percarbonates, perborates, persilicates and perphosphates. The per-salt is preferably sodium percarbonate ($2Na_2CO_3.3H_2O_2$) or sodium perborate.

The QAC's useful in the present invention must be biocidal and preferably contain non-halogen or non-halogenated counter ions. Examples of suitable QAC's include alkyl dimethylbenzyl ammonium chloride, e.g. tetradecyl(C_{14})dimethylbenzylammonium chloride, alkyl trimethylammonium chloride, e.g. C_{16}alkyltrimethylammonium chloride, dialkyldimethylammonium chloride, e.g. C_9alkyl- C_{11}alkyl- dimethyl ammonium chloride, and

cetrylpyridiniumchloride, and other biocidal QAC's with halogen or halogenated cations and/or halogenated anions though, for preparing storage stable solutions, the most preferred QAC's are the biocidal QAC's having non-halogen or non-halogenated cations and non-halogenated anions and include alkyl poly(oxyalkyl)ammonium propionates such as N,N-didecyl-N-methyl-poly(oxyethyl)ammonium propionates, alkyl or alkylaryl ammonium methosulphates such as alkyltrimethyl ammonium methosulphates or alkyldimethylbenzylammonium methosulphate, dialkylammonium methosulphates, alkyldimethylbenzylammonium saccharinates, quaternary ammonium ethosulphates, quaternary ammonium hydroxides, polypropoxyquaternary ammonium acetates and polypropoxyquaternary ammonium phosphates. Preferably, the alkyl groups are C_1-C_{30}, more preferably C_{10}-C_{20}, and most preferably C_{12}-C_{16}, alkyl groups. The oxyalkyl groups are preferably oxy(C_1-C_6)alkyl groups.

The compositions of the present invention are preferably presented in the form of a powdered solid, though the components of the composition may be conveniently compounded into, for example, a tablet which is readily dispersible in an appropriate volume of the appropriate solvent.

The compositions of the present invention may comprise other components, such as surfactants, sequestering agents and dispersants, which are well known in the art for assisting the composition to dissolve in the solvent.

The preferred solvents include water and appropriate organic polar solvents such as methanol or ethanol. Water is the most preferred solvent.

When the compositions of the present invention are dissolved in the solvents, the resultant solutions usually take an alkaline pH of about 9 to 11. Whilst the resultant solutions are extremely effective against microbes at these pH's, it is preferred that the solutions are made acidic, e.g. having a pH of from 1 to 7, preferably pH4, for enhanced storage stability. The solution may be made acidic by adding any acid, preferably a food acid such as citric, tartaric, adipic, succinic or glutaric acid, to the solution after the peracid has formed. The acid may be added to the solution preferably at a time to coincide with the maximum generation of peracid from the precursor and per-salt. As will be appreciated by the skilled person, the exact time for addition of the acid will depend upon the particular precursor/per-salt system, concentration of the precursor/per-salt system in the solvent, temperature and the pH of the solvent used, though typically, at ambient temperatures (20°C), the acid is added from about 5 up to about 15 minutes or more after the composition has been added to the solvent.

In an embodiment of the present invention, there is provided a tablet comprising a single solid acidic core, or a plurality of solid acidic cores, embedded in a solid per-salt. The core or cores are preferably coated with a slow dissolving layer, such as silicate, which enables a delayed release of the acid when the tablet is added to an appropriate solvent. The per-salt is preferably mixed with an organic acid precursor and, optionally, a biocidal QAC, preferably a biocidal QAC which has a non-halogen or non-halogenated cation. In practice, the tablet is added to a solvent, e.g. water, and the per-salt, and any precursor and QAC, is allowed to dissolve or disperse into the solvent. At this point in time, the solution has a pH of about 9 and is unstable for long periods of time. A few minutes later, e.g. after about 5 to 15 minutes when at ambient temperatures, to coincide with the maximum generation of peroxide or, when the precursor is present, to coincide with the maximum generation of peroxyacid, the acid is released from the core(s) into the solvent and the pH of the solution drops to about 4, thereby rendering the solution more time stable.

The compositions of the present invention may find use in a number of applications where cleaning, sanitising or sterilising solutions are required.

One particular use of the compositions is in the formation of a sterilizing solution which may be used by doctors or dentists to sterilise their instruments. The solutions of the present invention offer the advantage that sterilisation of surgical instruments and the like may be effected in a one step process, rather than a two step process as currently practiced with prior art sterilisation systems. The solutions based on the compositions may also be used in dairies, food processing plants, animal houses, dairy farms and breweries, where the rapid, broad spectrum activity of the compositions together with their ability to wet and penetrate give significant advantages over traditional sanitisers and disinfectants. The solutions may also be used in paper mills, where a disinfectant is required to prevent microbial growth in the papermaking processes.

The present invention will now be further described by reference to the following specific examples and Figure 1 and Figure 2.

Figure 1 and Figure 2 are graphs which demonstrate the fast acting effect as a microbicide of compositions of the present invention dissolved in water.

In a first series of experiments, five aqueous solutions were prepared by dissolving in water:

1. 0.2g of powdered PCS in 100ml of demineralised (DM) water,
2. 0.1g of powdered ARQUAD DM 14B-90 in 100ml of DM water,
3. 0.2g of powdered PCS and 0.1g of powdered ARQUAD DM 14B-90 in 100ml of DM water,
4. 0.2g of powdered PCS and 0.15g of powdered TAED in 100ml of DM water, and
5. 0.2g of powdered PCS. 0.15g of powdered TAED and 0.1g of powdered ARQUAD DM 14B-90 in 100ml of DM water.

The solutions were allowed to stand for 5 minutes at ambient temperature to allow perhydrolysis of the precursor to generate peroxyacid.

1.0ml of each of the solutions were then added to 1.0ml of a suspension of 10^7 cfu/ml *Candida lambica* contained in 8.0ml of DM water and the clock started.

The performance of the solutions as microbicides against *Candida lambica* was evaluated by comparing the LRF values and time from adding the 1.0ml aliquot of solution to the yeast suspension. The results are shown in Figure 1 (ARQUAD DM 14B-90 is a tetradecylbenzyldimethylammonium chloride available from Akzo)

In a second series of experiments, six aqueous solutions were prepared by dissolving in water:

1. 0.2g of powdered PCS in 100ml of demineralised (DM) water,
2. 0.1g of powdered ARQUAD DM 14B-90 in 100ml of DM water,
3. 0.2g of powdered PCS and 0.15g of powdered TAED in 100ml of DM water,
4. 0.2g of powdered PCS. 0.15g of powdered TAED and 0.1g of powdered ARQUAD DM 14B-90 in 100ml of DM water,
5. 0.3g of powdered STEPANQUAT F in 100ml of DM water, and
6. 0.2g of powdered PCS, 0.15g of powdered TAED and 0.1g of powdered ARQUAD DM 14B-90 in 100ml of DM water.

The procedure of the first series of experiments was repeated for the above solutions. The performance of the solutions as microbicides against *Candida pelliculosa* was evaluated as above by comparing the LRF values and time from adding the 1.0ml aliquot to the yeast suspension. The results are shown in Figure 2
(STEPANQUAT F is a non-biocidal QAC available from Stepan).

The surprising synergistic biocidal advantage of the compositions of the present invention in solution over the other solutions is readily seen from Figure 1 and Figure 2.

In a third series of experiments, the performance of 5 compositions as microbicides against *Candida lambica* was evaluated by determining the LRF over a period of a few minutes. The QAC used was ARQUAD DM 14B-90. The results are given in Table 1 below:

TABLE 1

Conc^n per litre	Log Reduction			
	1 min	3mins	5mins	10mins
0.2g PCS			1.9	2.8
			1.8	2.8
0.2gPCS + 0.15g TAED		2.2	3.4	4.2
			2.3	3.1
0.2gPCS + 0.2g SNOBS	4.5	5.5	>5.5	>5.5
	2.9	3.6	4.2	4.8
0.2gPCS + 0.15gTAED + 0.1g QAC	4.6	5.2	>5.5	>5.5
0.2gPCS + 0.15gTAED + 0.05g QAC	5.4	5.4	>5.5	>5.5
0.2gPCS + 0.2gSNOBS + 0.1g QAC	5.2	5.2	>5.5	>5.5
0.2gPCS + 0.2gSNOBS + 0.05g QAC	5.4	>5.5	>5.5	>5.5

In a forth series of experiments, the stability performance of two compositions of the present invention held over a period of 12 weeks are compared with one another. The results are shown in Table 2 below. The preference for using PBS instead of PCS can be readily seen. The QAC used was ARQUAD DM 14B-90.

TABLE 2

	30% PBS-1 20% TAED 20% QAC 50% Na_2SO_4		30% PCS 20% TAED 20%QAC 50% Na_2SO_4	
Week	%AvOx	% Loss	%AvOx	% Loss
0	1.94		1.79	
1	1.93	0.5	1.52	14.8
6	1.75	8.5	1.25	30.2
8	1.77	8.8	1.26	29.4
12	1.77	8.8	1.08	39.7

A tablet comprising a composition of the present invention may be prepared as follows:

Particles of citric acid are fed to an aeromatic and sprayed with a solution of sodium silicate to encapsulate the acid in a coating which is slowly soluble in water. The coating is effected at room temperature followed by drying at elevated temperature. Next, granules of PCS and TAED, together with a solution of PVA binding agent, are added to the coated acid particles and the mixture formed to a tablet and allowed to dry at elevated temperature. Each tablet comprised an acid core embedded in a solid PCS/TAED casing. The tablet was readily soluble in water over a period of 10 minutes, first the PCS/TAED being dissolved then, more slowly, the acid core was dissolved. The resulting solution had a pH of about 4 and was stable for at least 24 hours.

Claims

1. A solid composition suitable for use in preparing a cleaning, sanitizing or sterilising composition, characterised in that the composition comprises an organic peracid precursor, a per-salt and a biocidal quaternary ammonium compound (QAC).

2. A composition as claimed in claim 1, wherein the weight ratio of precursor: per-salt is from about 4:1 to about 1:20, preferably from about 1:1 to about 1:10, and more preferably from about 1:2 to about 1:5.

3. A composition as claimed in claim 1 or claim 2, wherein the weight ratio of precursor and persalt:QAC is from about 1:1 to about 1:30, preferably from about 1:1 to about 1:20, and most preferably from about 1:2 to about 1:10.

4. A composition as claimed in claim 1, claim 2 or claim 3, wherein the QAC has a non-halogen or non-halogenated anion, and preferably has a non-halogen or non-halogenated anion and a non-halogenated cation.

5. A composition as claimed in any one of the preceding claims, wherein the QAC is one or more compounds selected from the group consisting of alkyl poly(oxyalkyl)ammonium propionates such as N,N-didecyl-N-methyl-poly(oxyethyl)ammonium propionates, alkyl or alkylaryl ammonium methosulphates such as alkyltrimethyl ammonium methosulphates or alkyldimethylbenzylammonium methosulphates, dialkylammonium methosulphates, alkyldimethylbenzylammonium saccharinates, quaternary ammonium ethosulphates, quaternary ammonium hydroxides, polypropoxyquaternary ammonium acetates and polypropoxyquaternary ammonium phosphates.

6. A composition as claimed in any one of the preceding claims, wherein the per-salt is selected from the group consisting of percarbonates, perborates, persilicates and perphosphates, and is preferably sodium percarbonate ($2Na_2CO_3.3H_2O_2$) or sodium perborate.

7. A composition as claimed in any one of the preceding claims, wherein the precursor is tetra acetyl ethylene diamine (TAED), sodium nonanoyl oxy benzene sulphonate (SNOBS) or penta acetyl glucose (PAG).

8. Use of a composition as claimed in any one of claims 1 to 7 in the preparation of a cleaning, disinfecting, sanitising or sterilising composition.

9. A solution, preferably an aqueous solution, comprising the reaction product of a composition as claimed in any one of claims 1 to 7.

10. A solution as claimed in claim 9, wherein the solution also includes an acid, preferably selected from citric acid, tartaric acid, adipic acid, succinic acid and glutaric acid.

11. Use of a solution as claimed in claim 9 or claim 10 in or as a cleaning, disinfecting, sanitising or sterilising composition.

10

Patents Act 1977
Examiner's report to the Comptroller under section 17 (The Search Report)

Application number
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Relevant Technical fields

(i) UK Cl (Edition L) A5E EBB

(ii) Int Cl (Edition 5) A01N

Search Examiner
P N DAVEY

Databases (see over)

(i) UK Patent Office

(ii) ONLINE DATABASES: WPI

Date of Search
3 AUGUST 1993

Documents considered relevant following a search in respect of claims 1-11

Category (see over)	Identity of document and relevant passages	Relevant to claim(s)
A	WO 88/00795 A1 (GARCIN) see eg page 4	1 at least

jf - doc99\fil000664

Category	Identity of document and relevant passages	Relevant to claim(s)

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